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Radical Catalyzed Addition of di-*n*-Propylformal and Diethylacetal to Dimethyl Maleate

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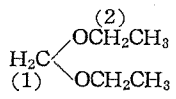
Continued from the previous research[1], the authors have investigated the radical-catalyzed reactions of di-*n*-propylformal and diethylacetal with dimethyl maleate respectively. In the former case the β-formylpropionic acid and in the latter case the acetylsuccinic acid and laevulic acid were detected as the reaction products. From these results it is suggested that, in the case of di-*n*-propylformal, the hydrogenatom of the methylene group of formaldehyde and in the case of diethylacetal, the hydrogenatom of the methylene group of ethylalcohol were abstracted by radical produced from benzoylperoxide. The authors have repeated again the reaction of orthoformate with dimethyl maleate and found an error in the previous report and here correction is made.

In the previous report[1] the authors made it clear that, in the radical-catalyzed addition reaction of diethylformal to dimethyl maleate, the hydrogenatom (2), not the hydrogen atom (1) of the diethylformal is abstracted by radical from benzoylperoxide

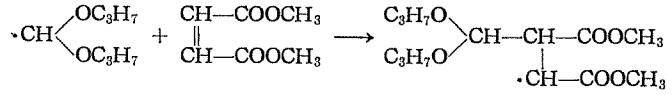


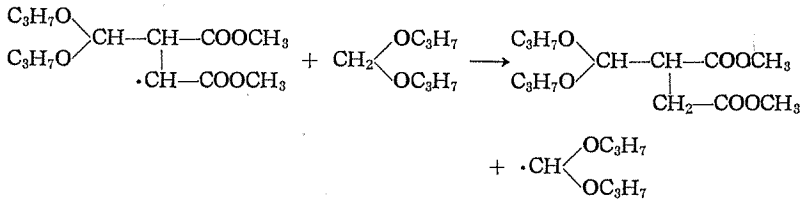
The authors have now undertaken a similar research using di-*n*-propylformal instead of diethylformal and quite unexpectedly found the β-formylpropionic acid as the final reaction product, i.e. after the hydrolysis of the 1 : 1-adduct. From this fact it is concluded, that the hydrogenatom (1), not the hydrogenatom (2) of di-*n*-propylformal was abstracted by the radical from benzoylperoxide, and that the reaction proceeded in the following manner :

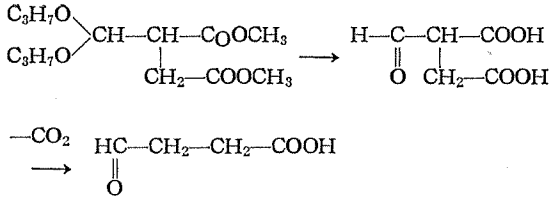
(1) $C_6H_5C(=O)-OO-C(=O)-C_6H_5 \longrightarrow R\cdot$

(2) $R\cdot + CH_2(OCH_2C_2H_5)_2 \longrightarrow RH + \cdot CH(OC_3H_7)_2$

* 永坂 晃, 中村 真三, 小田 良平

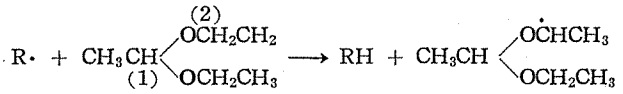
(3) 

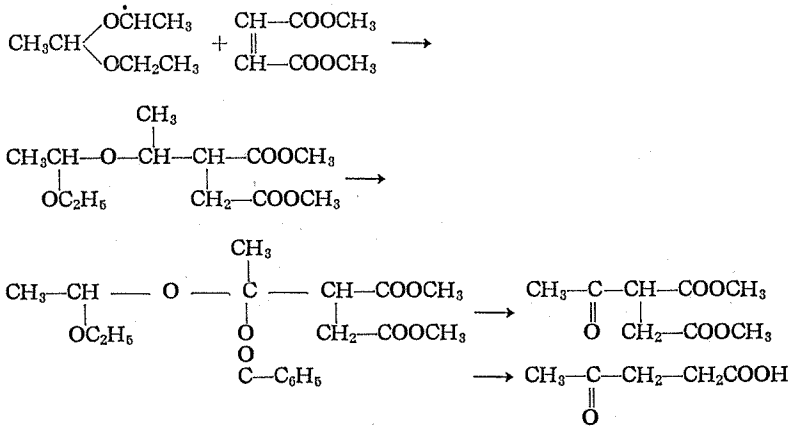
(4) 

(5) 

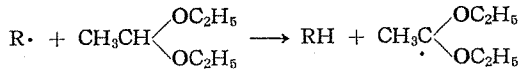
Next, the authors have performed the analogous experiment with diethylacetal and found the laevulic acid as the final reaction product. From this fact it is concluded that the reaction proceeded in this case in the following manners:

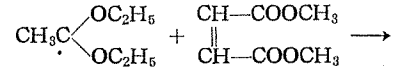
(6) benzoylperoxide $\longrightarrow$ R·

(7) 

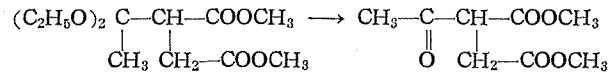
(8) 

or

(9) 

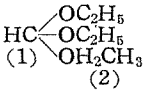
(10) 

Addition of Acetals to Dimethyl Maleate

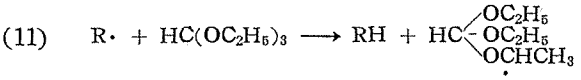


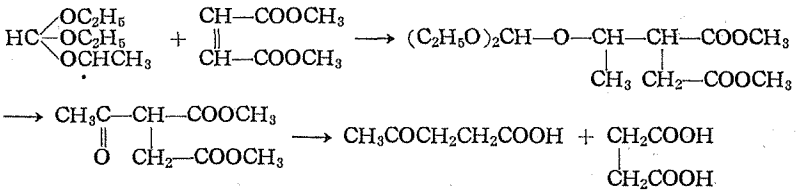
Thus, for the formation of acetylsuccinic acid, both the reactions (7) and (9), i.e. the abstraction of hydrogenatom (1) or (2) by the radical R· are considerable. It is difficult at present to determine, which of the above two courses is the true one.

Further, the authors have repeated again the reaction of orthoformate with dimethyl maleate, the result of which was reported in the previous paper[1]. This time the authors could detect the laevulic acid beside the succinic acid from the hydrolysate of the fraction (9) of the previous paper. In the previous experiment this laevulic acid was missed and it was suggested that only the hydrogenatom (1) of the orthoformate was abstracted.



But, this assumption was proved to be an error. On the contrary, for the formation of laevulic acid the hydrogenatom (2) of the orthoformate must be abstracted and the following reaction scheme is suggested reasonably.

(11) 

(12) 

After all, from the previous and the above results it is concluded that,

(i) in the case of diethylformal only the hydrogenatom (2) is abstracted,

(ii) in the case of orthoformate only the hydrogenatom (2) is abstracted,

(iii) in the case of di-*n*-propylformal only the hydrogenatom (1) is abstracted, and

(iv) in the case of diethylacetal either the hydrogenatom (1) or (2) is abstracted by the radical from the benzoylperoxide. The reason, why the reaction schemes in the above four cases are so different, though these four compounds are generally homologous in their chemical structures, is not clear to the authors at the present stage.

EXPERIMENTAL PART

I. The Reaction of di-*n*-Propylformal with Dimethyl-Maleate

Di-*n*-propylformal was synthesized after the method of Trillat[2]. Di-*n*-propyl-

formal (242 g), dimethyl maleate (90 g) and benzoylperoxide (22 g) were mixed and heated on a water bath in CO_2-stream for 10 hours. The reaction mixture was at first colorless and changed gradually into pale yellow. It was then rectified and the fractions boiling at 64～90° (ca. 4 g) and at 90～137° (ca. 205 g) were collected. The first fraction contained benzene, produced from phenylradical by abstracting hydrogen from di-*n*-propylformal and the second fraction was the unchanged di-*n*-propylformal. To the residue 350 ml benzene was added and this solution was extracted with soda-solution. From the soda-extract 4.5 g benzoic acid was obtained after acidification. After washing and drying, the benzene solution was distilled and the following fractions were obtained.

(1) 90～114°/16 mm, 14 g, colorless oil. This fraction was the unchanged dimethyl maleate.
(2) 115～145°/16 mm, 14 g, colorless oil.
(3) 146～165°/17 mm, 15.5 g, colorless oil.
(4) 155～188°/6 mm, 10 g, pale yellowish, viscous liquid, mol. wt. = 266.
(5) 188～205°/6 mm, 5.5 g, pale yellowish, viscous liquid, mol. wt. = 309.
(6) Residue, 24 g, brown semi-solid.

The fraction 3 was further rectified and the following fractions were obtained.

(3-1) 120～120.5°/6 mm, 2.5 g, colorless oil.
(3-2) 120.5～125°/6 mm, 6.5 g, colorless oil, mol, wt. = 183.
(3-3) 125～130°/6 mm, 4.5 g, colorless oil, mol. wt. = 191.

The (3-2) fraction was refluxed with 15 g HCl (20 %) for 1.5 hours and after concentration colorless crystal was obtained. This crystal was filtered and it was identified as succinic acid by mixed melting. From the filtrate of this succinic acid 2.4-dinitrophenylhydrazone of β-formylpropionic acid was obtained. This was identified by comparison with an authentic sample.

The fraction (3-3) was also hydrolyzed with HCl and after concentration of the hydrysate phenylsuccinic acid, succinic acid and β-formylpropionic acid were identified.

From fractions 4 and 5 no identifiable crystalline product was obtained.

From the values of molecular weight of the fractions (3-2) and (3-3), it may be suggested that precursors of these fractions were presumably di-*n*-propylacetal of formylsuccinic acid ester, which were hydrolyzed into formylsuccinic acid ester during the soda-treatment and this formylsuccinic acid ester was then converted into β-formylpropionic acid and succinic acid by refluxing with hydrochloric acid.

II. The Reaction of Diethylacetal with Dimethyl Maleate

The diethylacetal was synthesized after the method of Org. Synth[3]. A mixture of 190 g diethylacetal, 60 g dimethyl maleate and 15 g benzoylperoxide was heated in CO_2-stream on a water bath at 90～95° for 8 hours. The mixture was

rectified under ordinary pressure and fractions boiling at 68~86° (6.5 g) and 88 ~ 125° (158 g) were collected. The first fraction contained chiefly benzene and the second was the unchanged diethylacetal. The residual solution was diluted with benzene and washed with soda-solution. From the soda-solution ca. 3 g benzoic acid was obtained after acidification. The benzene solution was distilled after washing and drying and the following fractions were obtained.

(7) 74~84°/11 mm, 10 g, colorless oil. This fraction was the unchanged dimethyl maleate.

(8) 85~124°/10 mm, 9.5 g, colorless oil and needle crystal.

(9) 125~133°/9 mm, 5 g, colorless oil.

(10) 134~160°/8 mm, 2.5 g, pale yellowish oil.

The fraction (8) was dissolved in benzene and extracted again with soda-solution. From the soda-solution 2.5 g benzoic acid was obtained after acidification. The residual benzene solution was redistilled and the following fractions were obtained.

(8-1) 118~140°/38 mm, 2.5 g, colorless oil.

(8-2) 140~150°/38 mm, 3.5 g, colorless oil.

From the fraction (9) and (8-2) acetylsuccinic acid was detected as its phenylhydrazone respectively. From the fraction (10) phenylsuccinic acid was detected after hydrolyzing with conc. HCl.

III. The Reaction of Orthoformate with Dimethyl Maleate

A mixture of 190 g orthoformate, 70 g dimethyl maleate and 15g benzoylperoxide was heated at 90~95° in CO_2-stream for 11 hours. The reaction mixture was treated as already mentioned[1] and a fraction boiling at 126~135°/9mm was separated (4g ··· fraction 11). This fraction corresponds to the fraction, 100~118°/4 mm, of the previous report[1]. This fraction (3 g) was refluxed with 15 g of 20% HCl for 1.5 hours and concentrated. After cooling the succinic acid crystallized out similarly as the previous experiment. From the filtrate of this succinic acid the 2,4-dinitrophenylhydrazone of laevulic acid was detected and identified by comparing with an authentic sample. The molecular weight of the fraction (11) was measured and found as 221. From this value of molecular weight it is suggestable that the original fraction (11) is not the triethoxymethylsuccinic acid ester

$$(C_2H_5O)_3C—\underset{\displaystyle CH_2—COOCH_3}{\underset{|}{CH}}—COOCH_3 \quad ,$$

but the acetylsuccinic acid ester, and this compound was converted into a mixture of laevulic acid and succinic acid.

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(1) A.Nagasaka, This Bulletin, **32**, 238 (1954).

(2) M.M.A.Trillat, *Compt. rend.*, **118**, 1277 (1894).
(3) "Org. Synth". III, 1 (1923).